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(54) A METHOD OF PURIFYING CRUDE PETROLEUM
 AND PRIMARY REFINERY PRODUCTS

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 20 USSR, all state enterprises organised and
 existing under the laws of the Union of Soviet
 Socialist Republics (USSR), do hereby de-
 25 clare the invention, for which we pray that
 a patent may be granted to us, and the
 method by which it is to be performed, to be
 particularly described in and by the follow-
 ing statement:—
 This invention relates to methods of purify-
 30 ing crude petroleum and primary refinery pro-
 ducts, such as gasoline, jet fuel, diesel fuel,
 boiler oil and a wide cut from atmospheric
 and vacuum still distillation, from sulphur
 and sulphur compounds, nitrogen- and
 35 oxygen-containing compounds and naphthenic
 acids.
 The primary refinery products, after being
 purified, find widespread use as blending
 stocks for motor fuels, as jet fuels, boiler oil,
 40 and also as catalytic cracking feedstocks.
 The presence of sulphur impairs markedly
 the performance characteristics of motor
 gasolines, jet fuels and diesel oils. Active
 sulphur compounds, such as mercaptans and
 hydrogen sulphide, are highly corrosive agents
 so that their presence in fuels is not per-
 missible. Inactive sulphur compounds, such as
 disulphides, sulphides and thiophene, when
 present in fuels cause no corrosion of fuel-
 feed systems, but form, in the course of fuel
 combustion, highly corrosive combustion pro-
 ducts which are also detrimental in that they
 pollute the atmosphere.
 The employment of sulphur-bearing fuels
 reduces the engine life as a result of rapid
 wear of principal engine elements and also
 effects adversely engine efficiency.
 In this specification and in the claims
 "crude petroleum" describes petroleum after
 it has been dewatered and desalinated, in the
 form in which it is supplied to still distilla-
 60 tion furnaces, and "primary refinery products"
 are straight run gasoline, jet fuel, diesel fuel,
 furnace fuel and wide cut from atmospheric
 and vacuum still distillation.
 Nitrogen- and oxygen-containing compounds
 and naphthenic acids diminish fuel stability in
 storage due to gum formation, so that it is
 current commercial practice to carry out
 catalytic hydrofining of diesel oil, kerosenes
 and sometimes also of gasolines having
 70 medium and low content of sulfur. However,
 diesel oil hydrofining results only in the
 removal of mercaptans and in total sulphur
 diminution, the content of nitrogen- and
 oxygen-containing compounds undergoing no
 75 appreciable decrease, while the hydrofining of
 low-sulphur gasolines and kerosenes provides
 for an adequate removal of mercaptans, but
 exerts practically no effect on the total
 sulphur content.
 80

Hydrofining involves the destruction of organosulphur compounds accompanied by the formation of hydrogen sulphide. However, sulphur compounds containing chemically-active functional groups could be used as valuable raw materials in the preparative, synthetic and engineering fields of chemistry if a convenient method of isolating these compounds was available.

On the other hand, more stringent requirements as to the maximum permissible content of sulphur compounds in commercial petroleum products necessitate carrying out on an increasing scale the hydrofining of petroleum products, such as low-sulphur products. However, existing refineries possess, for the most part, limited facilities for petroleum product hydrofining, and moreover a scarcity of hydrogen prevents the capacity of hydrofining units from being expanded.

The situation outlined hereinabove demonstrates the necessity for developing methods for purify petroleum distillates of sulphur compounds.

No method has heretofore been available for the simultaneous removal of sulphur, sulphur-containing compounds, nitrogen- and oxygen-containing compounds and naphthenic acids from crude petroleum and primary refinery products such as gasoline, kerosine, diesel oil, fuel oil and boiler oil.

Our Patent No. 1,401,828 describes and claims a method of increasing the octane rating of petrol, which is a secondary refinery product, comprising mixing together petrol and a complex compound of a lower-valency transition metal, the complex compound being selected from transition metal carbonyls, complex compounds of transition metal compounds with n-type ligands and complex compounds of transition metal salts with strong reducing agents, heating the resulting mixture in a non-oxidising environment and separating the target product from the heated mixture. Such treatment removes diene hydrocarbons from the petrol.

It is an object of the present invention to provide a method of purifying crude petroleum and primary refinery products (virgin stocks) or sulphur, sulphur compounds, nitrogen- and oxygen-containing compounds and also of naphthenic acids which will make it possible to dispense with the conventional step of caustic treatment and subsequent hydrofining of said stocks or to avoid the purification process involving the use of oxygen-containing gases and aqueous solution.

According to the present invention there is provided a method of purifying crude petroleum and primary refinery products from sulphur, sulphur compounds, nitrogen- and oxygen-containing compounds and naphthenic acids, comprising reacting together in a homogeneous reaction mixture crude petroleum or

a virgin petroleum stock and a substance selected from π -complexes of transition metals as hereinafter defined, salts and π -allylic complexes of platinum metals, and carbonyl complexes of transition metals as hereinafter defined in a non-oxidising environment, and separating the purified product from the reaction mixture.

Preferably the treatment is performed at a temperature in the range from 80° to 150°C, most preferably from 80° to 120°C.

By the term "transition metals" is meant Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt.

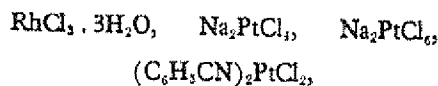
In the course of the treatment, sulphur compounds (hydrogen sulphide, sulphur, mercaptans, disulphides and thiophene), a part of nitrogen- and oxygen-containing compounds, and naphthenic acids react with the treating substance and form non-volatile compounds. From the resulting reaction mixture, the thus-purified target product may be isolated by distillation under atmospheric pressure, vacuum distillation or steam distillation, the aforementioned non-volatile compounds remaining behind as still bottoms.

It is further practicable to isolate the purified product by filtering the reaction mixture and thereafter passing the filtrate through an adsorbent-packed column containing, for example, silica gel, alumina, aluminosilicate, zeolite or activated charcoal, or filtering the filtrate through a thin bed of an adsorbent such as those specified above. Other suitable separation techniques include centrifugation and sedimentation.

In order to separate the purified product to maximum possible degree, it is expedient to treat the reaction mixture with a chelating agent which reacts with unconverted organometallic compounds to yield non-volatile and insoluble (in the petroleum products) compounds, thereby providing for a more complete separation of said compounds from the purified product.

Irrespective of the separation technique used, the metal content in the target product can be reduced to less than 0.0005% by weight.

Suitable π -complexes of transition metals are cyclopentadienylmetal carbonyls (Cr, Mo, W, Ni, Fe, Mn, V, and Co), dicyclopentadienyls of Cr, Ni, and Co, arenemetal carbonyls (Cr and Mo), bis-arene compounds of chromium, olefinemetal carbonyls (Fe, Co) and dienemetal carbonyls (Fe, Co). The preferred salts or π -allylic complexes of platinum metals are the salts or π -allylic complexes of Pt, Pd, Rh and Ir such for example as



bis - (π -allylrhodium chloride) and bis -

(π - allylpalladium chloride), while polynuclear Fe carbonyls and also Co, Ni, Cr, Mo, Mn and W carbonyls or mixtures thereof are the preferred carbonyl complexes of transition metals.

Preferable chelating agents are o - phenanthroline, α, α' - dipyridyl, acetylacetone and other β - diketones, and other chelating ligands capable of yielding strong complexes with the appropriate metal.

In order to effect the purification of kerosene or a wide cut boiling in the range from 30—35° to 230—235°C obtained on atmospheric and vacuum pipe stills, it is expedient to treat the kerosene or wide cut directly as it leaves the pipe still with a complex or salt of a transition metal, i.e., with a π -complexes of a transition metal, a salt or π -allylic complex of a platinum metal, or a carbonyl complex of a transition metal, dissolved in kerosene or a wide cut respectively, and separating the thus-purified target product from the reaction mixture by filtration through a bed of ferric oxide and aluminosilicate adsorbent taken in a 1:5 weight ratio.

To isolate the purified product, use can also be made of any technique described hereinabove.

The treatment yields hydrocarbon mixtures which are completely free of H₂S, S, mercaptan and disulphide sulphur, while the content of total sulphur in the mixture is decreased substantially (on the average, by a factor of from 2 to 6), and the concentration of nitrogen- and oxygen-containing compounds, naphthenic acids and other reactive admixtures diminishes by 20 to 50%.

The removal of the aforementioned impurities enhances significantly the marketability of the thus-treated petroleum products owing to improve odour, colour stability and gum formation resistance characteristics.

The method of the present invention is superior to previously-proposed processes by making it possible to carry out in a single stage the removal of sulphur, sulphur compounds, nitrogen- and oxygen-containing compounds and naphthenic acids from petroleum and primary refining products, dispensing with the use of hydrogen and catalysts, avoiding the step of pretreating the petroleum products with a caustic solution, obviating the necessity of using aqueous alkalines in the course of purification, and involving no consumption of large quantities of oxygen-containing gases and other strong oxidizing agents. The present invention provides a substantial economic effect as petroleum product purification can be carried out as a single-stage process employing relatively cheap reactants. Another advantage of the present method is associated with the fact that organosulphur compounds do no go to waste, but can be recovered for subsequent utilization in the petrochemical industry. For example,

where use is made of a column packed with an adsorbent to separate the purified target product, the adsorbent can thereafter be washed with a solvent, such as an alcohol or acetone, and the resulting solution of the complexes concentrated, treated with acids, e.g. HCl, and subjected to distillation which yields a mixture of mercaptans that can be utilized as desired.

The present method for the purification of hydrocarbon mixtures may, for example, be accomplished as follows.

The petroleum products to be purified are placed, together with a reagent (transition metal π -complex or salt), in a vessel furnished with a reflux condenser to form a homogeneous mixture, and the mixture is heated to a temperature of 80—120°C and maintained at this temperature for a period of from 15 minutes to 2 hours, followed by separating the purified target product by a conventional technique. When purified target product separation is effected by means of a chelating agent, the latter should be introduced into a hot or a cooled reaction mixture, which is next heated to a temperature of from 100° to 200°C and maintained at said temperature for a period of from 1 to 8 hours. Next the reaction mixture is filtered or distilled under reduced pressure or with steam in order to separate the purified target product.

The accompanying flow sheet illustrates schematically the present method for the continuous purification of petroleum products. Kerosene 1 or a wide cut 2 (initial boiling point, 30—35°C; end boiling point, 230—235°C), as it leaves an atmospheric and vacuum pipe still, is directed at a temperature of 100—120°C to the intake side of a pump 3 where it is mixed with a solution 4 of the aforementioned organometallic compounds in kerosene or the wide cut, respectively, said solution being prepared in a vessel 5. The resulting mixture is fed to a filter-separator 6 and an adsorber-clarifier 7, in which there occurs the separation of the purified target product 8.

Embodiments of the present invention will now be described by way of illustration in the following Examples. Qualitative and quantitative tests for sulphur, sulphur compounds and nitrogen- and oxygen-containing compounds in petroleum products were carried out by standard techniques.

Example 1

250 ml. of straight gasoline not subjected to caustic treatment and boiling in the 50—150°C range (total sulphur, 0.018 wt.%; mercaptan sulphur, 0.0065 wt.%, and elemental sulphur, 0.003 wt.%) is mixed with 0.18 g of pentacarbonyl iron and the stirred mixture is refluxed for 1.5 hours. The colour of the solution changes from dark green to brownish-red. The reaction mixture is then

allowed to cool to room temperature and filtered to separate the precipitate formed, and thereafter the filtrate is boiled with 0.2 g of α, α' -dipyridyl until the solution loses its colour completely. The chelating agent generally undergoes complete dissolution and then forms a red precipitate. The reaction mixture is subjected to steam distillation, and the organic layer of the condensate is separated and analysed for the content of total sulphur and mercaptan sulphur, the average analysis of the target product being as follows, % by weight: total sulphur, 0.007; mercaptan sulphur, 0.0003; free sulphur, none; pH of aqueous condensate, 5.40. The copper strip test shows no stains or discoloration.

Example 2

300 ml. of straight gasoline (boiling range, 80° to 140°C; analysis, % by weight: total sulphur, 0.043; mercaptan sulphur, 0.0084; free sulphur, 0.004) and 0.2 g nickelocene are heated, with stirring, to boiling for a period of one hour. The colour of the solution changes from dark green to brownish-red. Next 0.1 g of o-phenanthroline is added to the mixture and heating to 120°C is continued for an additional hour. The hot reaction mixture is then filtered through an activated alumina bed. The filtrate is a colourless, clear liquid. The doctor test is negative. The gasoline causes no copper strip discoloration.

Example 3

500 ml. of straight run gasoline (boiling range, 55° to 150°C; analysis % by weight: total sulphur, 0.025; mercaptan sulphur, 0.0071) and 0.3 g of bis(ethylbenzene)-chromium is boiled, with stirring, for a period of 20 minutes, after which 0.1 g of o-phenanthroline is added to the mixture. The resulting mixture is boiled for 1 hour, and thereafter the gasoline is distilled off. The resulting colourless clear liquid contains, on average, 0.008 wt.% of total sulphur and 0.001 wt.% of mercaptan sulphur. The copper strip test shows no stains or discoloration.

Example 4

250 ml. of kerosene jet fuel not subjected to caustic treatment (boiling range, from 140° to 230°C; analysis, % by weight: total sulphur, 0.17; mercaptan sulphur, 0.006) and 0.23 g of dodecacarbonyliron are heated to 100°C, with stirring, until the solution colour changes from dark green to dark brown. The duration of this step is 10 minutes maximum. The reaction mixture is allowed to cool to room temperature and filtered to separate the precipitate formed. The filtrate is heated, with vigorous stirring, on a water bath with 0.3 g of o-phenanthroline. The chelating

agent undergoes complete dissolution, there forms a red sediment and carbon monoxide evolves vigorously. Heating of the reaction mixture is continued until discoloration of the solution is almost complete. Next the reaction mixture is subjected to steam distillation to produce an organic layer of a colourless stable liquid containing, on average, 0.0087 wt.% of total sulphur and 0.0004 wt.% of mercaptan sulphur. The aqueous condensate has a pH of 4.64. The thus-treated kerosene withstands the copper strip test (stains and discoloration are absent). In the purified material the content of reactive nitrogen-containing compounds is decreased by 45% and that of naphthenic acid by 27% as compared to the kerosene feedstock.

Example 5

500 ml. of kerosene jet fuel not subjected to caustic treatment (boiling range, from 145° to 220°C; analysis, wt.%: total sulphur, 0.45; mercaptan sulphur, 0.01 and a mixture of 0.3 g cobalt carbonyl and 0.2 g of molybdenum carbonyl are heated at a temperature of 120°C for a period of two hours. The reaction mixture acquires a dirty green colour. 1 g of α, α' -dipyridyl is added, and the resulting mixture is heated for 1 hour. On being cooled, the solution is filtered through an aluminosilicate adsorbent. The thus-treated kerosene contains, on average, 0.17 wt.% of total sulphur and 0.0005 wt.% of mercaptan sulphur, and withstands the copper strip test (no stains or discoloration).

Example 6

250 ml. of kerosene not subjected to caustic treatment boiling range, 140—226°C; analysis, wt.%: total sulphur, 0.16; mercaptan sulphur, 0.0048) and 0.27 g of bis-(cyclopentadienyl) tricarbonyl tungsten are heated at 100°C for 40 minutes, with stirring, and 0.1 g of α, α' -dipyridyl are added. The resulting mixture is heated at 120°C. The kerosene distilled off under reduced pressure (a water jet pump) is a colourless clear liquid having the following sulphur content, % by weight: total sulphur, 0.04; mercaptan sulphur, 0.00005. The thus-treated kerosene withstands a copper strip test (no stains or discoloration).

Example 7

300 ml. of caustic-untreated diesel oil (boiling range, from 187° to 355°C; analysis, wt.%: total sulphur, 1.04; mercaptan sulphur, 0.0076) and 0.3 g of dodecacarbonyliron are heated at 100—110°C, with stirring, until the dark green colour of the solution changes to brownish-red.

Next 0.3 g of o-phenanthroline is added and the resulting mixture is heated at 100°C until the brownish-red colour vanishes. The

reaction mixture is cooled to room temperature and filtered through a sintered glass funnel with some finely crushed silica gel placed thereon. The thus-purified diesel oil contains, on average, 0.38 wt.% of total sulphur and 0.001 wt.% of mercaptan sulphur. The content of nitrogen-containing compounds and naphthenic acids is reduced by 37 wt.% and 23 wt.%, respectively, as compared to that of charge stock.

Example 8

500 ml. of caustic-untreated diesel fuel (boiling range, from 200° to 380°C; analysis, wt. %: total sulphur, 1.42; mercaptan sulphur, 0.009) and 0.4 g of cyclopentadienylcobalt-dicarbonyl are heated at 110°C for a period of 1.5 hours. 0.2 g of o-phenanthroline are added and the resulting mixture is heated to 130°C for about one hour. Next the hot solution is filtered through an activated charcoal bed, the filtrate being a colourless clear liquid. The doctor test is negative. The thus-purified diesel fuel withstands the copper strip test, no stains or discoloration).

Example 9

300 ml. of caustic-untreated diesel fuel (boiling range, from 190° to 360°C; analysis, wt. %: total sulphur, 1.20; mercaptan sulphur, 0.0092) and 0.3 g of powdered $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ are heated, while being vigorously stirred, at 120°C for a period of 2.5 hrs. To the hot solution is added 0.3 ml. of acetylacetone, and the mixture is stirred for an additional 0.5 hour at 100°C and filtered through an active alumina bed. The filtrate is a clear liquid containing less than 0.0001% of mercaptan sulphur.

Example 10

One litre of crude petroleum (total sulphur content, 1.73 wt.%) is heated with 10 g of dodecacarbonyliron at a temperature of 150°C for a period of 2 hours. 1 g of o-phenanthroline is then added and the resulting mixture is heated at the same temperature for one hour. Fractionation yields the following cuts:

I. From the initial boiling point to 150°C; 141 ml.; total sulphur content, 0.019 wt.%; mercaptan sulphur content, 0.0002 wt. %.

II. 150—235°C; 185 ml.; total sulphur, 0.031 wt.%; mercaptan sulphur, 0.0001 wt. %.

III. 240—350°C; 180 ml.; total sulphur, 0.42 wt.%; mercaptan sulphur, none.

All the three fractions withstand the copper strip test (no stains or discoloration).

Example 11

500 ml. of straight fuel oil (pour point, 19°C; relative viscosity at 80°C, 6.8; total sulphur content, 0.56 wt.%) is vigorously

stirred and heated at 150°C with 1 g of dodecacarbonyliron for a period of 2 hours. The hot solution is then filtered through an aluminosilicate adsorbent bed. The resulting product has an average content of total sulphur of 0.2 wt.% maximum. The treatment described hereinabove causes no change in the pour point, relative viscosity or ash content of the fuel oil feedstock.

Example 12

300 ml. of kerosene (total sulphur, 0.20 wt.%; mercaptan sulphur, 0.02 wt.%) and 0.2 g of bis- π -allylpalladium chloride) are heated at 80°C, while being stirred, for a period of 2 hours. Subjecting the reaction mixture to steam distillation yields kerosene containing 0.12 wt.% of total sulphur and 0.003 wt.% of mercaptan sulphur.

Example 13

400 ml. of straight gasoline (total sulphur, 0.03 wt.%; mercaptan sulphur, 0.009 wt.%) and 0.3 g of mesitylenemolybdenum tricarbonyl are boiled, with stirring, for a period of 2 hours. Vacuum distillation yields the target gasoline containing, on average, 0.009 wt.% of total sulphur and 0.0003 wt.% of mercaptan sulphur.

Example 14

250 ml. of kerosene (prior to caustic treatment, the content of total sulphur equals 0.23 wt.% and that of mercaptan sulphur 0.021 wt.%) and 0.22 g of a maleic anhydride-tetracarbonyliron complex are heated at a temperature of 120°C for a period of 1.5 hours. Filtering the hot reaction mixture through an aluminosilicate adsorbent bed yields a colourless clear liquid which contains, on average, 0.09 wt.% of total sulphur and 0.0007 wt.% of mercaptan sulphur.

Example 15.

300 ml. of diesel fuel (gas oil) containing 1.2 wt.% of total sulphur and 0.01 wt.% of mercaptan sulphur) and 0.4 g of cyclohexadieneirontricarbonyl are heated, with stirring, at a temperature of 100°C for a period of 2 hours. The hot reaction mixture is filtered through a silica gel bed. The resulting product contains, on average, 0.27 wt.% of total sulphur and 0.0005 wt.% of mercaptan sulphur.

Example 16.

Hot kerosene (mercaptan sulphur content, 0.0066 wt.%) from an atmospheric and vacuum distillation unit is passed through feedstock heat exchangers and mixed at a temperature of 105°C on the intake side of a pump with a solution of dodecacarbonyliron in kerosene prepared in a vessel, the concentration and volume of the solution being

selected so as to obtain in the kerosene to be purified a dodecacarbonyliron concentration of 0.2 g/l. From the pump, the reaction mixture is fed to one of alternately-operated filters-separators and thence comes to an adsorber-clarifier packed with ferric oxide (Fe_2O_3) and an aluminosilicate adsorbent taken in a weight ratio of 1:5. The properties of the thus-purified kerosene are listed in the Table.

Example 17

A hot wide cut (mercaptan sulphur content, 0.012 wt. %) having an initial boiling point of 30—35°C and an end boiling point of 230—235°C is directed, after passage through feedstock heat exchangers, to the intake side of a pump where it is mixed at

a temperature of 110°C with a solution of bis(ethylbenzene)chromium in the wide cut. The solution is prepared in a vessel in a concentration and used in an amount required to obtain in the wide cut to be purified a bis-(ethylbenzene)chromium concentration of 0.11 g/l. Next the mixture is fed to one of alternately-operated filters-separators and thence comes to an adsorber-clarifier packed with ferric oxide (Fe_2O_3) and an aluminosilicate adsorbent taken in a weight ratio of 1:5. The thus-purified wide cut (boiling range, from 30° to 230°C) is next directed to a secondary distillation unit for separation into a gasoline and a kerosene fraction. In the kerosene fraction, the content of mercaptan sulphur is diminished to 0.0003 wt.%. 20 25 30

TABLE

Property	Purified product	Charge stock
1. Density at 20°C, g/cm ³	0.775	0.7785
2. Fraction composition:		
initial boiling point, °C	137	132
10% is collected at °C	155	152
50% is collected at °C	176	174
90% is collected at °C	208	208
98% is collected at °C	222	222
3. Kinematic viscosity, centistoke		
a) at 20°C	1.30	1.28
b) at 40°C	5.12	5.194
4. Smoke point, mm	28	26
5. Acidity, mg KOH per 100 ml. of fuel	0.21	0.21
6. Flash point (close-cup test) °C	28	29
7. Initial crystallization point, °C	-60	-61
8. Iodine number, g per 100 g of fuel	1.2	1.28
9. Content of aromatics, wt. %	15.6	17
10. Thermal stability at 150°C during 4 min. mg per 100 ml. of fuel	6.0	6.4
11. Lower calorific capacity, kcal/kg	10,375	10,355
12. Actual gum content, mg per 100 ml. of fuel	2.0	1.5
13. Sulphur content, wt. %	0.09	0.17
14. Mercaptan sulphur content, wt. %, maximum	0.000258	0.0066
15. Hydrogen sulphide content	None	None
16. Naphthenic acid soaps	None	None
17. Copper strip test	Passed	Passed
18. Content of water-soluble acids and bases	None	None
19. Ash content, wt. %	None	None
20. Mechanical impurities and water	None	None

WHAT WE CLAIM IS:—

1. A method of purifying crude petroleum and primary refinery products from sulphur, sulphur compounds, nitrogen- and oxygen-containing compounds and naphthenic acids, comprising reacting together in a homogeneous reaction mixture crude petroleum or a virgin petroleum stock and a substance selected from π -complexes of transition metals as hereinbefore defined, salts and π -allylic complexes of platinum metals, and carbonyl complexes of transition metals as hereinbefore defined in a non-oxidising environment, and

separating the purified product from the reaction mixture. 80

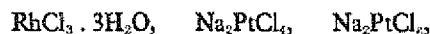
2. A method as claimed in claim 1, wherein the treatment is performed at a temperature in the range from 80° to 150°C.

3. A method as claimed in claim 2, wherein the treatment is performed at a temperature in the range from 80°C to 120°C. 85

4. A method as claimed in claim 1, 2 or 3, wherein the treating substance is a π -complex of a transition metal selected from nickelocene, bis - (ethylbenzene) chromium, 90

bis - cyclopentadienyl tungstentricarbonyl, and cyclopentadienylcobaltdicarbonyl.

5. A method as claimed in claim 1, 2 or 3, wherein the treating substance is a salt of a platinum metal selected from



and



6. A method as claimed in claim 1, 2 or 3, wherein the treating substance is a π -allylic complex of a platinum metal selected from bis - (π - allylrhodiumchloride) and bis-(π -allylpalladiumchloride).

7. A method as claimed in claim 1, 2 or 3, wherein the treating substance is a carbonyl complex of a transition metal selected from polynuclear Fe carbonyls, carbonyls of Co, Ni, Cr, Mo, W and Mn and mixtures thereof.

8. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100° to 200°C, and distilling off the desired product.

9. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100° to 200°C, and filtering the thus-treated reaction mixture through an active alumina bed.

10. A method as claimed in claim 8, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100° to 200°C, followed by steam distillation.

11. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100° to 200°C, and filtering the thus-treated reaction mixture through an aluminosilicate adsorbent bed.

12. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100° to 200°C, and filtering the thus-treated reaction mixture through a silica gel bed.

13. A method as claimed in claim 8, wherein the purified product is separated from the reaction mixture by treating the reaction

mixture with a chelating agent at a temperature of from 100° to 200°C, and subjecting the thus-treated reaction mixture to vacuum distillation.

14. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by treating the reaction mixture with a chelating agent at a temperature of from 100 to 200°C, and filtering the thus-treated reaction mixture through an activated charcoal bed.

15. A method as claimed in any of claims 8 to 14, wherein the chelating agent is selected from o-phenanthroline, α, α' - dipyridyl and acetylacetone.

16. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by steam distillation.

17. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by vacuum distillation.

18. A method as claimed in claims 1 to 7, wherein the purified product is separated from the reaction mixture by filtering the reaction mixture through an aluminosilicate adsorbent bed.

19. A method as claimed in any of claims 1 to 7, wherein the purified product is separated from the reaction mixture by filtering the reaction mixture through a silica gel bed.

20. A method as claimed in claim 1, 2 or 3, wherein the charge stock being purified is kerosene from an atmospheric and vacuum petroleum distillation unit and the purification comprises treating the kerosene as it leaves said distillation unit with a complex or salt of a transition metal in the form of a solution in the kerosene, and separating the purified product from the thus-obtained reaction mixture by filtering the reaction mixture through a bed of ferric oxide admixed with aluminosilicate adsorbent taken in a weight ratio of 1:5, respectively.

21. A method as claimed in claim 1, 2 or 3, wherein the charge stock being purified is a wide cut having an initial boiling point of 30—35°C and an end boiling point of 230—235°C from an atmospheric and vacuum petroleum distillation unit and the purification comprises treating the wide cut as it leaves said distillation unit with a complex or salt of a transition metal in the form of a solution thereof in the wide cut, and separating the purified product from the thus-obtained reaction mixture by filtering the reaction mixture through a bed of ferric oxide admixed with aluminosilicate adsorbent taken in a weight ratio of 1:5, respectively.

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22. A method of purifying crude petroleum and primary refinery products substantially as hereinbefore described with reference to any of Examples 1 to 17.
- 5 23. Purified petroleum and petroleum products obtained by the method claimed in any of the preceding claims.

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